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(71) Applicant (*for all designated States except US*): MCA TECHNOLOGIES GMBH [CH/CH]; Bruckackerstrasse 48, CH-4105 Biel-Benken (CH).

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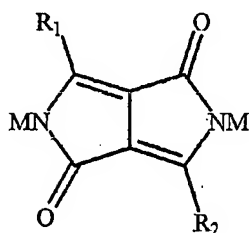
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(71) Applicant and

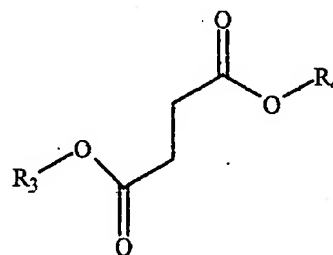
(72) Inventor: KAUL, Bansil, Lal [CH/CH]; Bruckackerstrasse 48, CH-4105 Biel-Benken (CH).

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(54) Title: SOLVENT-FREE PROCESS FOR THE PREPARATION OF PYRROLO (3,4C) PYRROLE COMPOUNDS



(I)



(II)

R<sub>1</sub>-CN (II)

or

R<sub>2</sub>-CN (III)

(57) Abstract: The invention relates to a *novel essentially-solvent-free process* for the preparation of 1,4-diketopyrrolo-[3,4-c]pyrrole compounds of general formula (I) in which both M represent hydrogen or an alkali metal, both R<sub>1</sub> and R<sub>2</sub> represent independently of the other an isocyclic or a heterocyclic aromatic radical, which process is characterized by reacting 1 mole of a disuccinate II wherein each R<sub>3</sub> and R<sub>4</sub> independently of the other is an alkyl or a cycloalkyl or an aryl radical, with 2 moles of a nitrile of the formula R<sub>1</sub>-CN (III) or R<sub>2</sub>-CN (IV) or a 2 mole mixture of the nitrile of formula (III) and the nitrile of the formula (IV), *essentially in the absence of any organic solvent* and in the presence of a strong base at elevated temperature, and obtaining the compound of formula (I) from the reaction product by subsequent hydrolysis when M represents hydrogen. Formulae (I, II). R<sub>1</sub>-CN (II) or R<sub>2</sub>-CN (III).

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## SOLVENT-FREE PROCESS FOR THE PREPARATION OF PYRROLO (3,4C) PYRROLE COMPOUNDS

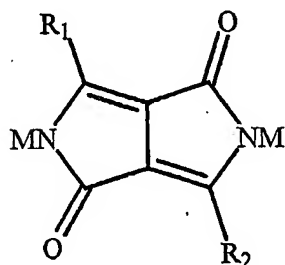
### Description

The present invention relates to a particularly advantageous process for the preparation of 1,4-diketopyrrolo[3,4-c]pyrrole compounds, to the products obtained by such process and to their use as valuable pigments.

A process for the synthesis of 1,4-diketo-3,6-diphenylpyrrolo[3,4-c]pyrroles starting from benzonitrile and ethyl bromoacetate in the presence of activated zinc-copper couple is described in Tetrahedron Lett. 1974, 2549-52. However, the yields obtained up to now have been unsatisfactory.

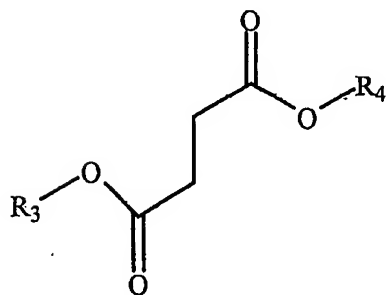
By starting from a succinate and an aromatic nitrile under specific reaction conditions as described in United States Patent 4,579,949 the desired pyrrolo[3,4-c]pyrroles are obtained in substantially higher yield. However, the process requires the use of very special inert organic solvents. To obtain high yields as claimed in the patent, besides being inert, the solvents need to be of high purity and particularly substantially anhydrous. Furthermore, the solvents need to be regenerated for reuse after their use in the process. Regeneration of solvents in high purity and particularly in substantially anhydrous form makes the process further cumbersome. Moreover, the use of solvent also reduces the productivity and requires higher energy consumption thereby making the process less economical. For example, the United States Patent 4,579,949 also describes the use of 5 to 20 parts by weight of solvent per 1 part by weight of reactants. Other disadvantages of a solvent based process include environmental (VOC), hygiene and safety issues.

Accordingly, the present invention provides a process for the preparation of 1,4-diketopyrrolo[3,4-c]pyrroles of the formula I



I

wherein both M represent an alkali metal and each of  $R_1$  and  $R_2$  independently of the other is an isocyclic or heterocyclic aromatic radical, which process comprises reacting 1 mole of a disuccinate II



II

wherein each  $R_3$  and  $R_4$  independently of the other is an alkyl or a cycloalkyl or an aryl radical, with at the most 2 moles of a nitrile of the formula

$R_1$ -CN (III)

or

$R_2$ -CN (IV)

or with 0.1 to 1.9 mole of a nitrile of the formula (III) and 1.9 to 0.1 mole of the nitrile of the formula (IV), essentially in the absence of any organic solvent and in the presence of a strong base at elevated temperature.

Suitable strong bases include alkali metals such as lithium, sodium and potassium, an alkali metal amide, an alkali metal hydride; and alkali metal or alkaline earth metal alkoxides derived in particular from primary, secondary or tertiary aliphatic alcohols having 1 to 10 carbon atoms. It is also possible to use a mixture of the above mentioned alkali metal alkoxides. Preference is given to using alkali metal alkoxides with alkali metal being especially sodium or potassium, and the alkoxide is preferably derived from a secondary or tertiary alcohol. Particularly preferred strong bases are for example sodium tert-butyrate and sodium tert-amylate. These alkali metal alkoxides can also be prepared in situ by reacting the corresponding alcohol with alkali metal.

If an alcoholate is used as a base, it may also be used as a solution or a suspension in the same alcohol or in an inert solvent. The alcohol and/or the solvent thus used and formed during the reaction may continuously be distilled off during the reaction thereby providing solvent-free reaction conditions. It may be advantageous when the disuccinate contains the same or similar alkyl groups as the alcoholate.

In the process of the invention, the strong base can be used in an amount from 0.8 to 4 mol,

preferably from 1.0 to 2.5 mol, based on 1 mole of the nitrile compound used.

The radicals  $R_1$  and  $R_2$  of the nitriles of the formula (III) and (IV) may be different or identical, but are preferably identical.  $R_1$  and  $R_2$  as isocyclic aromatic radicals are preferably monocyclic to tetracyclic radicals, most preferably monocyclic or bicyclic radicals, i.e. phenyl, biphenyl or naphthyl. Heterocyclic aromatic radicals  $R_1$  and  $R_2$  are preferably monocyclic to tricyclic radicals. These radicals may be entirely heterocyclic or may contain a heterocyclic ring and one or more fused benzene rings, and the cyano group can be linked both to the heterocyclic and to the isocyclic moiety respectively. Examples of heterocyclic aromatic radicals are: pyridyl, pyrimidyl, pyrazinyl, triazinyl, furyl, pyrrolyl, thiophenyl, quinolyl, benzimidazolyl, quinazolyl, quinoxalyl, phthalazinyl, phthalazindionyl, phthalamidyl, isoquinolinyl, isothiazolyl, acridinyl, acridonyl, quinazolidionyl, quinoxalindionyl, benzoxazindionyl, benzoxazinonyl and naphthalimidyl.

Both the isocyclic and the heterocyclic aromatic radicals may contain the customary non-watersolubilising substituents such as:

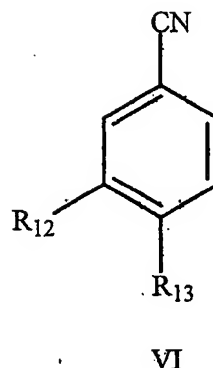
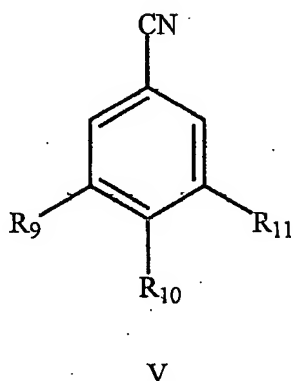
- (1) Halogen atoms, e.g. chlorine, bromine or fluorine atoms.
- (2) Branched or unbranched alkyl groups containing preferably 1 to 18, especially 1 to 12, more particularly 1 to 8 and, most preferably, 1 to 4 carbon atoms. These alkyl groups may contain non-watersolubilising substituents, e.g. fluorine,  $-\text{OCOR}_5$ ,  $-\text{OR}_6$ ,  $-\text{CONR}_7$  or  $-\text{CONHR}_8$ , wherein  $R_5$  and  $R_6$  are alkyl, aryl such as naphthyl, or benzyl or benzyl substituted by halogen, alkyl or alkoxy, or a heterocyclic radical;  $R_7$  and  $R_8$  are hydrogen, alkyl or alkyl substituted by cyano or hydroxy, or  $\text{C}_7 - \text{C}_8$  cycloalkyl, aryl or heteroaryl, especially phenyl or phenyl substituted by halogen, alkyl or alkoxy, or  $R_7$  and  $R_8$  together with the nitrogen atom form a 5- or 6-membered heterocyclic ring, e.g. a morpholine, piperidine or phthalimide ring. Further possible substituents at the alkyl groups are mono- or dialkylated amino groups, aryl radicals such as naphthyl or preferably phenyl or phenyl substituted by halogen, alkyl or alkoxy, or also heterocyclic aromatic radicals such as 2-thienyl, 2-benzoxazolyl, 2-benzthiazolyl, 2-benzimidazolyl, 6-benzimidazolonyl, 2-, 3- or 4-pyridyl, or 2-, 4- or 6-quinolyl radicals.
- (3) Alkoxy groups containing preferably 1 to 18, especially 1 to 12, more particularly 1 to 8 and, most preferably, 1 to 4 carbon atoms.
- (4) A cyano group.

Examples of unsubstituted or substituted alkyl groups are: methyl, ethyl, n-propyl, isopropyl, n-butyl, sec-butyl, tert-butyl, tert-amyl, n-pentyl, n-hexyl, 1,1,3,3-tetramethylbutyl, n-heptyl, n-octyl, nonyl, decyl, undecyl, dodecyl, hydroxymethyl, trifluoromethyl, trifluoroethyl, cyanomethyl, methoxycarbonylmethyl, acetoxymethyl or benzyl.

Preferred meanings of  $R_1$  and  $R_2$  are phenyl or phenyl substituted by one or two fluorine, chlorine or bromine atoms or mixtures thereof, by one, two or three methoxy or methyl groups or mixtures thereof with chlorine atoms, by cyano, by dimethylamino, by trifluoromethyl, by alkoxycarbonyl of 2 to 3 carbon atoms, by tert-butyl, by cyanophenyl, by acetyl or by alkylbenzoyloxy of 11-14 carbon atoms; biphenyl; naphthyl or naphthyl substituted by methoxy; anthryl; phenanthryl; pyridyl or pyridyl substituted by methyl or by amyloxy; quinolyl; furyl or thienyl.

It is also preferred to use nitriles of the formulae III and/or IV, wherein  $R_1$  and  $R_2$  are unsubstituted phenyl or naphthyl or phenyl or naphthyl which contain non-watersolubilising substituents.

In particular, the starting materials employed are nitriles of the formula V



wherein each of  $R_9$ ,  $R_{10}$  and  $R_{11}$  independently of one another is hydrogen, fluorine, chlorine, bromine, cyano, trifluoromethyl,  $C_1$ - $C_{12}$  alkyl,  $C_1$ - $C_{12}$  alkoxy,  $C_1$ - $C_{12}$  alkylmercapto,  $C_2$ - $C_{13}$  alkoxy carbonyl,  $C_2$ - $C_{13}$  alkanoylamino,  $C_1$ - $C_{12}$  monoalkylamino,  $C_2$ - $C_{24}$  dialkylamino or phenoxy, phenylmercapto, phenoxycarbonyl, phenylcarbamoyl or benzoylamino, each unsubstituted or substituted by halogen,  $C_1$ - $C_{12}$  alkyl or  $C_1$ - $C_{12}$  alkoxy, with the proviso that at least one of  $R_9$ ,  $R_{10}$  and  $R_{11}$  is hydrogen.

Most preferably, the starting materials employed are nitriles of the formula VI wherein one of  $R_{12}$  and  $R_{13}$  is chlorine, bromine,  $C_1$ - $C_4$  alkyl, cyano,  $C_1$ - $C_4$  alkoxy, or phenoxy, carbamoyl or  $C_2$ - $C_5$  alkylcarbamoyl, each unsubstituted or substituted by chlorine or methyl, or phenylcarbamoyl which is unsubstituted or substituted by chlorine, methyl or methoxy, and the other is hydrogen.

The disuccinates II to be used in the process of this invention may be dialkyl, dicycloalkyl or diaryl. The dialkyl, dicycloalkyl and diaryl succinates may also be unsymmetrical. However, it is preferred to use symmetrical disuccinates, most preferably symmetrical dialkyl succinates.

Examples of disuccinates are dimethyl succinate, diethyl succinate, dipropyl succinate, dibutyl succinate, dipentyl succinate, dihexyl succinate, diheptyl succinate, dioctyl succinate, diisopropyl succinate, di-sec-butyl succinate, di-tert-butyl succinate, di-tert-amyl succinate, di-[1,1-dimethylbutyl] succinate, di-[1,1,3,3-tetramethylbutyl] succinate, di-[1,1-dimethylpentyl] succinate, di-[1-methyl-1-ethylbutyl] succinate, di-[1,1-diethylpropyl] succinate, diphenyl succinate, di[4-methylphenyl] succinate, di-[2-methylphenyl] succinate, di-[4-chlorophenyl] succinate, monoethyl-monophenyl succinate, and dicyclohexyl succinate.

The disuccinates II and the nitriles of the formula III or IV are known compounds and may be prepared by known methods.

The process of the invention is carried out in the absence of any solvent in the temperature range from 70° C to 200° C, with the preferred range being from 80° to 140° C.

It is entirely possible to carry out the process of the invention not only batchwise, but also continuously. When using disuccinates containing alkyl radicals and alcoholates which are derived from lower alcohols such as methanol, ethanol, n-propanol, isopropanol or tert-butanol, it may be necessary to remove the lower alcohol formed during the reaction from the reaction medium continuously in order to obtain higher yields.

A further preferred embodiment of the process consists in using the nitrile to be reacted with the disuccinate in no more than the stoichiometric proportions. It has been found that the yield of final product can usually be further improved by using an excess of disuccinate over the nitrile, in which case the optimum amount must be determined according to the respective reactants and may be up to 50 per cent in excess over the stoichiometric amount required with respect to the nitrile.

According to a further feature of the invention, 1,4-diketopyrrolo[3,4-c]pyrroles of the formula I wherein both M represent hydrogen are obtained from the corresponding pigment alkali metal salts by hydrolysis with water and or an alcohol in the presence or absence of an organic and/or an inorganic acid known in the art such as described in United States Patent 6,375,732. For example, suitable hydrolysis methods include dropping the alkali metal salt into water or an alcohol. The water and/or alcohol can be used in any desired mixing ratio between 5 and 20 parts by weight per 1 part of the pigment alkali metal salts used. The presence of a mineral acid such as sulfuric acid or an organic acid, such as acetic acid, in the water and/or an alcohol is advantageous in such precipitation methods.

In a preferred method, the solvent used for hydrolysis is an alcohol, in particular a primary or a secondary alcohol. Preferred alcohols are C<sub>1</sub> to C<sub>8</sub> alcohols such as methanol, ethanol, n-propanol, isopropylalcohol, butanol, iso-butanol and especially iso-octanol. The water and/or alcohol can be used in any desired mixing ratio between 5 and 20 parts by weight per 1 part of the pigment alkali metal salt to be hydrolysed. Water or butanol/water mixtures are particularly suitable for drowning the pigment salts suspension.

Depending on the pigments and on the hydrolysis conditions, pigments with a particle size below 1.5 microns possessing the required pigmentary properties are thus obtained.

One can also use additives known in the state-of-the-art to control the particle size of the pigment composition. It is possible as well to control the particle size of the pigment composition by heating under pressure the final pigment suspension following the hydrolysis.

When the finishing of the pigment is complete, the conditioned pigment is isolated by filtration, with the presscake being washed with water or an organic solvent, preferably methanol, followed by water and dried. Good results can be obtained by performing the filtration in acidic conditions.

1,4-Diketopyrrolo[3,4-c]pyrroles of the formula I wherein both M represent hydrogen and which are particularly useful as organic pigments, can be generated and simultaneously auto-dispersed in situ in the water and/or alcohol borne substrates from the compounds of formula I wherein both M represent alkali metal, by hydrolysis. This process has the advantage that the final dispersion in the medium of incorporation is obtained with a fine particle size and excellent dispersion without having to use any special milling equipment.

Depending on the end-use, the pigments obtained by the process of the invention can be

converted into a more opaque or more transparent form. To obtain a transparent form, the hydrolysis is preferably carried out at lower temperature (below 80° C).

If it is desired to obtain a more opaque pigment form, it is convenient to carry out a hydrolysis at more elevated temperature (above 80° C), with or without pressure. It is also possible first to isolate the pigment after the hydrolysis and then to heat it in water or an organic solvent, with or without pressure, in order to obtain the opaque form. It is preferred to employ an organic solvent having a boiling point above 80° C. Particularly suitable solvents are benzenes which are substituted by halogen atoms or by alkyl or nitro groups, e.g. xylenes, chlorobenzene, o-dichlorobenzene or nitrobenzene, as well as pyridine bases such as pyridine, picoline or quinoline, and also ketones such as cyclohexanone, ethers such ethylene glycol monomethyl or monoethyl ether, amides such as dimethylformamide or N-methylpyrrolidone, and also dimethylsulfoxide or sulfolane. The aftertreatment may also be carried out in water in the presence of an organic solvent and/or with the addition of surface-active compounds.

Depending on the envisaged end-use, it may be advantageous to prepare mixtures of compounds of the formula I wherein both M represent hydrogen. This can be done for example by mixing different 1,4-diketopyrrolo[3,4-c]pyrroles of the formula I wherein both M represent alkali metal and which have been prepared independently of one another before the hydrolysis, hydrolysing them together and then isolating the resultant mixture of compounds of the formula I wherein M represent hydrogen. It is also possible to hydrolyse two or more compounds of the formula I together.

Depending on the nature of their substituents and on the polymers to be coloured, the compounds of formula I may also be used as polymer-soluble colourants. Normally, however, the compounds of formula I are used as pigments for organic materials of high molecular weight and can be used in general directly in the form in which they are obtained by the process of this invention.

Organic materials of high molecular weight which may be pigmented with the compounds of formula I are e.g. cellulose ethers and esters such as ethyl cellulose, nitrocellulose, cellulose acetate, cellulose butylate, natural resins or synthetic resins such as polymerisation resins or condensation resins, e.g. aminoplasts, in particular urea/formaldehyde and melamine/formaldehyde resins, alkyd resins, phenolic plastics, polycarbonates, polystyrene, polyvinyl chloride, polyolefins such as polyethylene, polypropylene, polyacrylonitrile, polyacrylates, polyamides, polyurethanes or polyesters, rubber, casein, silicone and silicone resins, individually or in mixtures.

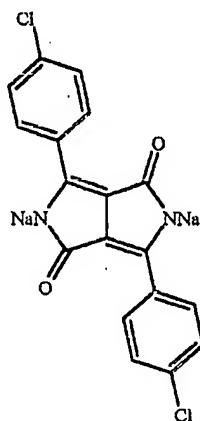
It is immaterial whether the above organic compounds of high molecular weight are in the form of plastics, melts or of spinning solutions, lacquers, paints or painting inks. Depending on the end-use, it is advantageous to use the pigments of this invention in the form of toners or formulations. The compounds of the formula I are employed in an amount of preferably 0.01 to 10% by weight, based on the organic material of high molecular weight to be pigmented.

The colorations obtained, e.g. in plastics, filaments, lacquers or printing inks, have excellent tinctorial strength, good dispersibility, good fastness to overspraying, migration, heat, light and atmospheric influences, as well as good gloss.

There now follows a series of examples which serves to illustrate the invention.

### Example 1

2475 g of p-chlorobenzonitrile, 2181.6 g diisopropyl succinate and 2869.2 g sodium tert-butylate are placed at 20-25° C in a 10000 ml "All In One Reactor"® of (Drais Mannheim Germany). Under stirring and nitrogen flow the mixture is heated to 100° C within 60 minutes. From 80° C onwards the reaction mixture becomes considerably thicker and is finally converted into a paste. From 80-85° C onwards a rapid formation of alcohol vapours is observed. The temperature is maintained at 99° to 100° C for three hours, thereby allowing the mixture of isopropyl alcohol and tert-butyl alcohol to distil off. The reaction mass becomes crumbly and finally largely disintegrates into an almost semi-powdery material. The reaction mixture is heated to 120° C in 30 minutes and kept at 120° C for 30 minutes. The mixture is cooled to 50° C. The material is emptied into a polyethylene sack, tightly fitted to the outlet of the reactor; affording 3248 g (90 % of theory, based on p-chlorobenzonitrile) of pigment of the formula VI. Approximately 200 g (5.54 % of theory, based on p-chlorobenzonitrile) of the product are still contained in the reactor to be used in the next batch. The total yield thus corresponds to approximately 3448 g (approximately 95.54 % of theory, based on p-chlorobenzonitrile).



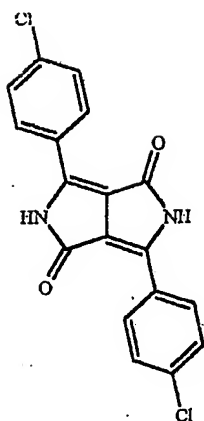
VI

This product produces an intense red colour when stirred into a state-of-art waterborne paint system.

### Example 2

For the hydrolysis, 1000 g product of the example 1 are slowly added to a mixture of 7000 ml of methanol and 35 g of acetic acid at room temperature. The mixture is then heated to reflux and kept at reflux temperature for two hours. The resultant pigment suspension is filtered at about 50° C, washed with methanol and water until the washings run colourless, and dried at 80° C in vacuum, affording 845 g (95 % of theory, based on compound of formula VI) of pure pigment of the formula VII



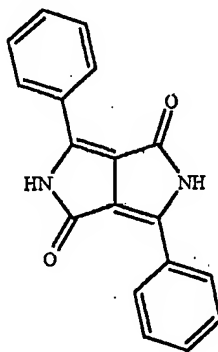


VII.

which colours PVC red.

### Example 3

1545 g of benzonitrile, 2242.5 g di-tert-butyl succinate and 3024 g potassium tert-butyrate are placed at 20-25° C in a 10000 ml "All In One Reactor" of (Drais Mannheim Germany). Under stirring and nitrogen flow the mixture is heated to 100° C within 60 minutes. From 70° onwards the reaction mixture becomes considerably thicker and is finally converted into a paste. From 70-75° onwards a rapid formation of alcohol vapours is observed. The temperature is maintained at 99 degree to 100° C for three hours thereby allowing the tert-butyl alcohol to distil off. The reaction mass becomes crumbly and finally largely disintegrates into an almost semi-powdery material. The reaction mixture is heated to 120° C in 30 minutes and kept at 120° C for 30 minutes. The mixture is cooled to 50° C. The material is emptied into a polyethylene sack, tightly fitted to the outlet of the reactor and then worked up as in example 2 yielding 1840 g (85% of theory, based on benzonitrile) of pure pigment of the formula VIII



VIII

### Example 4

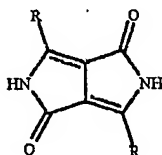
2750 g of p-chlorobenzonitrile and 2950 g sodium iso-propylate are placed at 20-25° C in a 10000 ml "All In One Reactor"® of (Drais Mannheim Germany). Under stirring and nitrogen flow the mixture is heated to 90° C within 60 minutes. As soon as this temperature has been reached, 2424 g diisopropyl succinate are added over 145 minutes by means of a metering pump. The temperature is kept constantly at 98-99° C and isopropyl alcohol is distilled off. The temperature is maintained at 99 to 100° C for two hours. The reaction mixture is heated to 120° C in 30 minutes and kept at 120° C for 30 minutes. The mixture is cooled to 50° C. The material is emptied into a polyethylene sack, tightly fitted to the outlet of the reactor; the yield is 3490 g (approximately 87% of theory, based on p-chlorobenzonitrile) of the compound of formula VI.

For the hydrolysis, 1000 g of the above reaction mixture is slowly added to 10000 ml of water at 80° C temperature. The resultant pigment suspension is heated to 95° C and kept at 95° C for two hours. Thereafter, it is filtered at about 80° C, washed with water until the washings run colourless, and dried at 80° C in vacuum; affording 872 g (98 % of theory, based on the compound of formula VI) of a very finely divided pigment of the formula VII.

The crude pigment is then finished by treating with seven volume parts of dimethyl formamide at 130° C for three hours. The suspension is filtered at 100° C, washed with the same volume of dimethyl formamide heated to 100° C followed by water at 70° C. The presscake is dried at 100° C yielding a bright red product.

### Examples 5-15

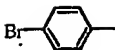
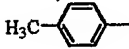
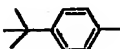
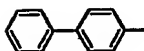


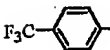



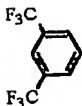
2 kilo mole of a nitrile of the formula R-CN, wherein R has the meaning indicated in Table 1, and 3960 g of sodium tert-amylate are placed at 20-25° C in a 10000 ml paddle drier (TurbuDry®, Drais Mannheim Germany). The mixture is heated under nitrogen to the temperature indicated in Table 1. As soon as this temperature has been reached, 2626 ml of di-isopropyl succinate are added by means of a metering pump over the period of time also indicated in Table 1 and with continuous stirring. The indicated temperature is maintained and the alcohol mixture formed is allowed to distil off. When the addition is complete, the reaction mixture is kept at the same temperature for 2 hours and hydrolysed and worked up as in Example 2 to give the pigments of the formula IX



IX

wherein R has the meaning given in Table 1, in the indicated yield.

Table 1

Example	R	Reaction Temperature in °C	Addition Time in minutes	Yield based on nitrile	Shade in PVC (0.1%)
5		98-100	120	81.7	red
6		90-92	130	75.9	red
7		95-97	180	73.2	orange
8		105-110	240	62.1	reddish violet
9		90-95	100	51.1	yellowish red
10		105-110	120	58.3	red
11		107-112	110	61.7	red
12		95-97	90	25.6	orange
13		90-92	60	45.5	red
14		90-95	90	32	red
15		99-100	63	37	red

## EXAMPLES 16-20

1.0 kilo mole of a nitrile of the formula  $R'-CN$  and 1.0 kilo mole of the formula  $R''-CN$ , wherein  $R'$  and  $R''$  are different and are as defined in Table II (Examples 16-20) and 3.4 kilo mole of sodium tert-amylate are placed at 20-25° C in a 10000 ml "All In One Reactor" ® (of Drais Mannheim Germany). By means of a metering pump, 1.2 kilomoles of diisopropyl succinate are added at the reaction temperature indicated in Table II over the period of time also indicated therein, while continuously distilling off the alcohol mixture. When the addition is complete, the mixture is kept for 2 hours at the reaction temperature and then hydrolysed and worked up as in Example 2 to give the pigment mixture of the formulas X, XI and XII

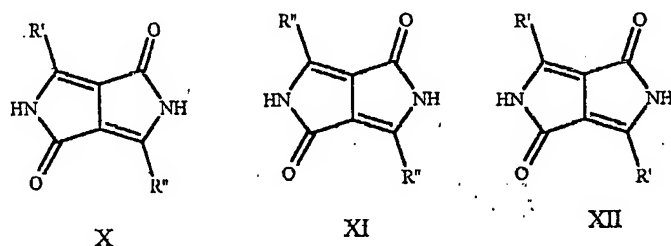


TABLE II

Example	$R'$	$R''$	Reaction Temperature °C	Yield in % of nitrile	Shade in PVC (0.2%)
16			95-100	69.7	red
17			90-95	57.7	scarlet
18			105-110	39.6	bluish red
19			90-95	82.7	red
20			110-115	67	orange

#### APPLICATION IN PVC MASSTONE

The preparation of a 0.1% colored PVC sheet is performed as follows: 100 parts of clear PVC are mixed with 0.1 part of pigment obtained according to Example 2 for 2 minutes. The mixture is passed between two rollers for 5 minutes, the front roller being heated at 130° C and the rear roller being heated at 135° C. Then the sheet is pressed under a pressure of 25 tons between two chromium-plated steel plates heated at 165° C, for 5 minutes. The pressed sheet is colored with a red shade.

#### APPLICATION IN PVC WHITE REDUCTION

The preparation of a 0.1% colored PVC sheet with white is performed as follows: 100 parts of PVC-white (containing 5%  $\text{TiO}_2$ ) are mixed with 0.1 part of pigment for 2 minutes. The mixture is passed between two rollers for 8 minutes, the front roller being heated at 160° C and the rear roller being heated at 165° C. Then the sheet is pressed under a pressure of 25 tons between two chromium-plated steel plates heated at 160° C, for 5 minutes.

#### APPLICATION IN COATINGS MASSTONE

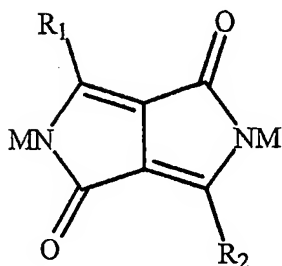
The preparation of an alkydmelamine resin coating is performed as follows: 3.6 g of pigment, 26.4 g of clear alkydmelamine paint (35%) and 85 g of glass beads are stirred in a Skandex stirrer for 30 minutes. 30 g of this preparation are mixed with 60 g of clear alkydmelamine paint (55.8%). The dispersion is sprayed on a cardboard sheet, air-dried for 15 minutes and baked at 140° C in an oven for 30 minutes.

#### APPLICATION IN COATINGS WHITE REDUCTION

The preparation of an alkydmelamine resin coating is performed as follows: 3.6 g of pigment, 26.4 parts of clear alkydmelamine paint (35%) and 85 g of glass beads are stirred in a Skandex stirrer for 30 minutes. 7.5 g of this preparation are mixed with 20 g of alkydmelamine white paint (containing 30%  $\text{TiO}_2$ ). The dispersion is sprayed on a cardboard sheet, air-dried for 15 minutes and baked at 140° C in an oven for 30 minutes.

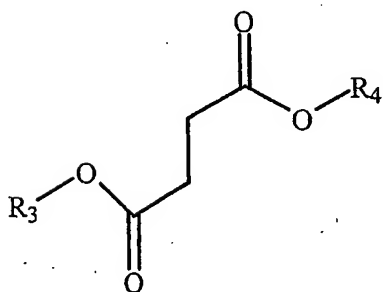
## Claims

1. Essentially solvent-free process for the preparation of 1,4-diketopyrrolo-[3,4-c]pyrrole compounds of general formula (I)



I

in which both M represent hydrogen or an alkali metal, each of  $R_1$  and  $R_2$  independently of the other is an isocyclic or heterocyclic aromatic radical, characterised by condensing an unsymmetrical or symmetrical dialkyl or diaryl succinate, or monoalkyl monoaryl succinate or dicycloalkyl succinate of formula II



II

wherein each  $R_3$  and  $R_4$  independently of the other is an alkyl or a cycloalkyl or an aryl radical, with two moles of nitrile of formula III

$R_1$ -CN (III)

or of formula IV

$R_2$ -CN (IV)

for at least each mole of succinate or with 0.1 to 1.9 mole of a nitrile of the formula (III) and 1.9 to 0.1 mole of the nitrile of the formula (IV), essentially in the absence of any organic solvent and in the presence of 2 to 5 moles of a strong base at a temperature of 70° to 200° C to yield compounds of formula I wherein M is an alkali metal; and optionally hydrolysing compounds of formula I or a mixture thereof, wherein M is an alkali metal to compounds of formula I or a mixture thereof, wherein M is hydrogen, in water, a lower alkanol, a mineral acid or an organic acid.

2. A process according to claim 1, wherein essentially no solvent is present at all.
3. A process according to claim 1, wherein said strong base is an alkali metal, an alkali metal amide, an alkali metal hydride, an alkali metal alcoholate or an alkaline earth metal alcoholate.
4. A process according to claim 1, wherein the nitrile is a single nitrile of the formula III or IV.
5. A process according to claim 1, wherein the disuccinate II is a symmetrical dialkyl succinate containing 1 to 18 carbon atoms in each alkyl moiety.
6. A process according to claim 1, wherein the disuccinate II is a symmetrical dialkyl succinate, wherein alkyl is sec- or tert-alkyl.
7. A process according to claim 1 wherein each of R<sub>1</sub> and R<sub>2</sub> independently of the other is phenyl or phenyl substituted by one or two chlorine atoms, by one or two methyl groups, by methoxy, by trifluoromethyl, by cyano, by methoxycarbonyl, by tert-butyl, by dimethylamino or by cyanophenyl; naphthyl; biphenyl; pyridyl or said pyridyl substituted by amyloxy; furyl or thienyl.
8. A process according to claim 7 wherein each of R<sub>1</sub> and R<sub>2</sub> independently of the other is phenyl, 3-chlorophenyl, 4-chlorophenyl, 3,5-dichlorophenyl, 4-methylphenyl, 4-methoxyphenyl, 3-trifluoromethylphenyl, 4-trifluoromethylphenyl, 3-cyanophenyl, 4-cyanophenyl, 4-methoxycarbonylphenyl, 4-tert-butylphenyl, 4-dimethylaminophenyl, 4-(p-cyanophenyl)phenyl, 1-naphthyl, 2-naphthyl, 4-biphenyl, 2-pyridyl, 3-pyridyl, 4-pyridyl, 6-amyloxy-3-pyridyl, 2-furyl or 2-thienyl.
9. A process according to claim 1, wherein the strong base is an alkali metal alcoholate.
10. A process according to claim 9, wherein the alkali metal alcoholate is derived from a secondary or tertiary alcohol.
11. 1,4-diketopyrrolo-[3,4-c] pyrroles of the formula I as prepared by the processes of claim 1 to claim 10.
12. Use of 1,4-diketopyrrolo-[3,4-c]pyrroles prepared by the processes of claim 1 to claim 10 for the mass pigmentation of substrates, preferably synthetic polymers, synthetic resins and regenerated fibres.
13. Use of 1,4-diketopyrrolo-[3,4-c]pyrroles prepared by the processes of claim 1 to claim 10 for the colouration of printing inks and textiles.

14. Use of 1,4-diketopyrrolo-[3,4-c]pyrroles prepared by the processes of claim 1 to claim 10 for the colouration of electrographic toners and developers.
15. Use of 1,4-diketopyrrolo-[3,4-c]pyrroles prepared by the process of claim 1 to claim 10 for the colouration of coatings.



## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/IB 03/00758

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07D487/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 962 499 A (CIBA SC HOLDING AG) 8 December 1999 (1999-12-08) the whole document	1-10
A	US 4 579 949 A (IQBAL ABUL ET AL) 1 April 1986 (1986-04-01) cited in the application the whole document	1-10
A	US 4 931 566 A (SURBER WERNER ET AL) 5 June 1990 (1990-06-05) the whole document	1-10

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*&amp;\* document member of the same patent family

Date of the actual completion of the international search

14 July 2003

Date of mailing of the international search report

16. 10. 03

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Fritz, M

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB 03/00758

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this International application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-10

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

## INTERNATIONAL SEARCH REPORT

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-10

Process for the preparation the compounds (I)

2. Claim : 11

Compounds (I)

3. Claims: 12-15

Use of the compounds (I) for the mass pigmentation of substrates.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 03/00758

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